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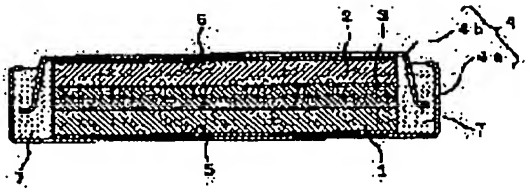
## (54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To improve a charging/discharging characteristic in a nonaqueous electrolyte secondary battery using metal compound which can store/release lithium ion for positive electrode active material in a positive electrode and also provide an excellent charging/discharging cycle characteristic.
SOLUTION: In a nonaqueous electrolyte secondary battery which has a positive electrode 1 using metal compound which can store/release lithium ion for positive electrode active material and a negative electrode 2 using lithium as active material and nonaqueous electrolyte, LiaCObMncMdNi1-(b+c+d)O2 (wherein, M is at least one kind of element selected from a group of Y, B, Al, Si, Ti, Fe, V, Cr, Cu Zn, Ga, Ge, Rb, Rh, Pd and W and a-d satisfy condition of 0<a<1.2, 0<b<0.5, 0<c<0.4, 0<d<0.4, 0<b+c+d<0.5) is used as the metal compound in the positive electrode.



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CLAIMS

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[Claim(s)]
[Claim 1] In the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which used for positive active material the occlusion of a lithium ion, and the metallic compounds which can be emitted, the negative electrode which uses a lithium as an active material, and nonaqueous electrolyte As metallic compounds in the above-mentioned positive electrode, it is Lia Cob Mnc Md nickel1-(b+c+d) O2 (M among a formula). It is a kind of element chosen from the group which consists of Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W at least. a-d 0<a<1. -- 2 and 0 -- < -- b< 0.5 and 0<c<0. -- 4 and 0 -- < -- the conditions of d< 0.4 and 0<b+c+d<0.5 are fulfilled. The nonaqueous electrolyte rechargeable battery characterized by using.
[Claim 2] It sets to the nonaqueous electrolyte system rechargeable battery indicated to claim 1, and is above metallic-compounds Lia Cob Mnc Md nickel1-(b+c+d) O2. Nonaqueous electrolyte rechargeable battery with which the value of a-d which can be set is characterized by fulfilling the conditions of 0< a<1.2, 0< b<0.5, 0< c<0.2, 0< d<0.2, and 0<b+c+d<0.5.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which used for positive active material the occlusion of a lithium ion, and the metallic compounds which can be emitted, the negative electrode which uses a lithium as an active material, and nonaqueous electrolyte, and relates to the nonaqueous electrolyte rechargeable battery which improved the above-mentioned positive electrode and has improved the cycle property especially.
[0002]
[Description of the Prior Art] In recent years, as one of the new style rechargeable batteries of high power and a high energy consistency, nonaqueous electrolyte is used for an electrolyte and oxidation of a lithium and the nonaqueous electrolyte rechargeable battery using reduction of high electromotive force came to be used.
[0003] as what the occlusion of a lithium ion and the metallic compounds which can be emitted are generally used, and can perform occlusion of a lithium ion, and emission efficiently especially as positive active material in the positive electrode in such a nonaqueous electrolyte rechargeable battery here -- LiNiO2 and LiFeO2 etc. -- the lithium-transition-metals multiple oxide with which kind content of the transition metals, such as Co, nickel, Fe, Mn, and Cu, was carried out at least was used for Li like.
[0004] However, in order to manufacture the ingredient in which the discharge engine performance may change greatly with the manufacture approaches, and the charge-and-discharge property that repeatability is good and fixed is shown, even if these lithium-transition-metals multiple oxides needed to set up manufacture conditions very strictly, and the manufacture was very troublesome and they were the ingredients which carried out in this way and were manufactured, when they repeated charge and discharge and performed it, they had the problem that where of a charge-and-discharge property deteriorates remarkably.
[0005] In the case of the multiple oxide containing nickel, in the above-mentioned lithium-transition-metals multiple oxide here nickel2+ ion compares with nickel3+ ion. Since it is stable, when mixing of baking conditions or a raw material is not uniform, LiNiO2 Not but, NiO came to be generated, and in connection with charge and discharge, the crystal structure of this multiple oxide changed gradually, turbulence and the absorption emission capacity of a lithium ion declined, and when it carried out by repeating charge and discharge as mentioned above, the charge-and-discharge property deteriorated remarkably.
[0006] For this reason, in recent years, as shown in JP,8-37007,A, in the lithium nickel complex oxide which contains nickel as mentioned above, the thing which made a part of this nickel permute from Co and Mn was developed.
[0007] Thus, although the nonaqueous electrolyte rechargeable battery in which the charge-and-discharge property that repeatability is good and fixed is shown is obtained and the cycle property also came to improve in the lithium nickel complex oxide containing nickel when some nickel is made to permute from Co and Mn When carried out by repeating charge and discharge, Mn which permuted some nickel was gradually eluted in nonaqueous electrolyte, cell capacity fell

by this, and there was a problem that sufficient charge-and-discharge cycle property was not acquired.

[0008]

[Problem(s) to be Solved by the Invention] The positive electrode which used for positive active material the metallic compounds which this invention emits [ the occlusion of a lithium ion and ], It is what makes it a technical problem to solve the above problems in the nonaqueous electrolyte rechargeable battery equipped with the negative electrode which uses a lithium as an active material, and nonaqueous electrolyte. In the nonaqueous electrolyte rechargeable battery which used for positive active material the lithium-transition-metals multiple oxide which contains nickel especially, while the charge-and-discharge property that repeatability is good and fixed is shown It is rare for cell capacity to fall by the increment in the number of cycles of charge and discharge, and let it be a technical problem to acquire the outstanding charge-and-discharge cycle property.

[0009]

[Means for Solving the Problem] In the nonaqueous electrolyte rechargeable battery in this invention In the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which used for positive active material the occlusion of a lithium ion, and the metallic compounds which can be emitted, the negative electrode which uses a lithium as an active material, and nonaqueous electrolyte in order to solve the above technical problems As metallic compounds in the above-mentioned positive electrode, it is Lia Cob Mnc Md nickel1-(b+c+d) O2 (M among a formula). It is a kind of element chosen from the group which consists of Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W at least. a-d $0<a<1$. -- 2 and $0 -- < -- b< 0.5$ and $0<c<0$. -- 4 and $0 -- < --$ the conditions of $d< 0.4$ and $0<b+c+d<0.5$ are fulfilled. It was made to use.

[0010] Namely, it sets to the nonaqueous electrolyte rechargeable battery in this invention. LiNiO2 In the lithium-transition-metals multiple oxide which contains nickel like While the charge-and-discharge property which permuted a part of that nickel from Co and Mn, was made to stabilize the crystal structure of this lithium-transition-metals multiple oxide, and repeatability fixed well is acquired Furthermore, by permuting a part of the nickel at least by a kind of element chosen from Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W It controls that Mn is gradually eluted in nonaqueous electrolyte, it prevents that cell capacity falls by this, and sufficient charge-and-discharge cycle property was acquired.

[0011] and as metallic compounds in a positive electrode like the nonaqueous electrolyte rechargeable battery in this invention Lia Cob Mnc Md nickel1-(b+c+d) O2 It is expressed. It is a kind of element chosen from the group which M becomes from Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W at least. If a-d uses $0< a<1.2$, $0< b<0.5$, $0< c<0.4$, $0< d<0.4$, and the thing that fulfills the conditions of $0<b+c+d<0.5$, while the charge-and-discharge property which repeatability fixed well will be acquired The fall of the cell capacity at the time of carrying out by repeating charge and discharge also decreases, and the nonaqueous electrolyte rechargeable battery excellent in the charge-and-discharge cycle property comes to be obtained.

[0012] Here, it is above metallic-compounds Lia Cob Mnc Md nickel1-(b+c+d) O2. The value of a-d which can be set Having fulfilled the conditions of $0< a<1.2$, $0< b<0.5$, $0< c<0.4$, $0< d<0.4$, and $0<b+c+d<0.5$ It is LiNiO2 by the increment in the amount [ as opposed to / are for a charge-and-discharge cycle property to fall remarkably, when not fulfilling one of these conditions, and / nickel in this ] of permutations. It is thought that it is because the phase of an except begins to appear.

[0013] Moreover, if it makes it hit that the charge-and-discharge cycle property in the nonaqueous electrolyte rechargeable battery of this invention improves further, it is above Lia Cob Mnc Md nickel1-(b+c+d) O2. It is desirable that the value of a-d which can be set fulfills the conditions of $0< a<1.2$, $0< b<0.5$, $0< c<0.2$, $0< d<0.2$, and $0<b+c+d<0.5$. This will be considered to be for the permutation element expressed with Mn or the above-mentioned M to dissolve to nickel more effectively if the value of a-d fulfills such conditions.

[0014] Moreover, in the nonaqueous electrolyte rechargeable battery in this invention, as a

negative-electrode ingredient used for the negative electrode which uses a lithium as an active material, the well-known negative-electrode ingredient currently used conventionally can be used, for example, carbon materials other than a metal lithium or a lithium alloy, such as occlusion of a lithium ion, a graphite which can be emitted, corks, and an organic substance baking object, can be used.

[0015] In the nonaqueous electrolyte rechargeable battery in this invention furthermore, also as the above-mentioned nonaqueous electrolyte Can use the well-known nonaqueous electrolyte currently used conventionally, and as a solvent in this nonaqueous electrolyte For example, ethylene carbonate, propylene carbonate, butylene carbonate, Vinylene carbonate, cyclopentanone, a sulfolane, a dimethyl sulfolane, The 3-methyl -1, 3-oxazolidine-2-ON, gamma-butyrolactone, Dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, Methylpropyl carbonate, butyl methyl carbonate, ethyl propyl carbonate, organic solvents, such as butyl ethyl carbonate, dipropyl carbonate, 1, 2-dimethoxyethane, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, methyl acetate, and ethyl acetate, -- one sort -- or two or more sorts can be used, combining.

[0016] moreover, the solute currently generally conventionally used in this nonaqueous electrolyte also as a solute dissolved in the above-mentioned solvent -- it can use -- for example, LiPF6, LiCF3 SO3, LiBF4, LiAsF6, LiN (CF3 SO2)2, and LiC (CF3 SO2)3 etc. -- it can be used.

[0017]

[Example] While giving an example and explaining concretely the nonaqueous electrolyte rechargeable battery concerning this invention hereafter, in the nonaqueous electrolyte rechargeable battery concerning this example, the example of a comparison is given and it is shown clearly that a charge-and-discharge cycle property improves. In addition, the nonaqueous electrolyte rechargeable battery in this invention is not limited to what was shown in the following example, in the range which does not change that summary, is changed suitably and can be carried out.

[0018] (Examples 1-6 and examples 1-7 of a comparison) In the nonaqueous electrolyte rechargeable battery in these examples 1-6 and the examples 1-7 of a comparison, the lithium cell which became a flat coin form as shown in drawing 1 was produced using the positive electrode, the negative electrode, and nonaqueous electrolyte which were produced as follows.

[0019] In producing [production of positive electrode] positive electrode LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 aluminum3 (OH) It uses. After mixing in a mortar so that it may become a mole ratio as Li:nickel:Co:Mn:aluminum shows in the following table 1, These were heat-treated at 750 degrees C under the dry air ambient atmosphere for 20 hours, respectively, an Ishikawa style stone mill mortar ground after that, and each positive active material with which mean particle diameter was set to about 1 micrometer was obtained.

[0020] next, each positive electrode with which the acetylene black which is an electric conduction agent, respectively, and the polyvinylidene fluoride which is a binder were added, and the acetylene black which is positive active material and an electric conduction agent, and the polyvinylidene fluoride which is a binder became the weight ratio of 90:6:4 to each positive active material which carried out in this way and was obtained, respectively -- the mixture was obtained.

[0021] and each positive electrode which carried out in this way and was obtained -- a mixture -- respectively -- 2 t/cm2 After carrying out pressurization molding by the pressure disc-like [ with a diameter of 20mm ], under the vacuum, it heat-treated at 250 degrees C for 2 hours, and each positive electrode was produced.

[0022] In producing [production of negative electrode] negative electrode, the rolled plate of a lithium-aluminium alloy was pierced to disc-like [ with a diameter of 20mm ], and the negative electrode was produced.

[0023] It is LiPF6 to the mixed solvent with which ethylene carbonate and dimethyl carbonate were mixed by the volume ratio of 1:1 in producing [production of nonaqueous electrolyte] nonaqueous electrolyte. It was made to dissolve at a rate of 1 mol/l, and nonaqueous electrolyte was produced.

[0024] In producing [production of cell] cell As shown in drawing 1 , while attaching in the positive-electrode charge collector 5 each positive electrode 1 produced as mentioned above Attach the above-mentioned negative electrode 2 in the negative-electrode charge collector 6, respectively, and the above-mentioned nonaqueous electrolyte is infiltrated into the separator 3 which consisted of polypropylene of lithium ion permeability. Form this separator 3 between each above-mentioned positive electrode 1 and a negative electrode 2, and this is made to hold in the cell case 4 formed by positive-electrode can 4a and negative-electrode can 4b. While connecting a positive electrode 1 to positive-electrode can 4a through the positive-electrode charge collector 5, a negative electrode 2 is connected to negative-electrode can 4b through the negative-electrode charge collector 6. This positive-electrode can 4a and negative-electrode can 4b were electrically insulated with the insulating packing 8, and each lithium cell of the examples 1-6 which became a coin form, and the examples 1-6 of a comparison was produced.
[0025] Next, it is each lithium cell of the examples 1-6 produced as mentioned above and the examples 1-7 of a comparison, respectively Charging current 0.5 mA/cm2 After making it charge to charge termination electrical-potential-difference 4.25V, Discharge current 0.5 mA/cm2 It was made to discharge to discharge-final-voltage 2.75V, carried out by having repeated charge and discharge by making this into 1 cycle, and asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 1.
[0026]
[Table 1]

| | 正極活物質（モル比） | | | | | サイクル数 |
|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Al | (回) |
| 実施例1 | 1.000 | 0.950 | 0.040 | 0.005 | 0.005 | 191 |
| 実施例2 | 1.000 | 0.950 | 0.005 | 0.040 | 0.005 | 185 |
| 実施例3 | 1.000 | 0.950 | 0.005 | 0.005 | 0.040 | 188 |
| 実施例4 | 1.000 | 0.950 | 0.020 | 0.010 | 0.020 | 179 |
| 実施例5 | 1.000 | 0.950 | 0.020 | 0.020 | 0.010 | 182 |
| 実施例6 | 1.000 | 0.950 | 0.010 | 0.020 | 0.020 | 176 |
| 比較例1 | 1.000 | 1.000 | 0.000 | 0.000 | 0.000 | 12 |
| 比較例2 | 1.000 | 0.950 | 0.050 | 0.000 | 0.000 | 13 |
| 比較例3 | 1.000 | 0.950 | 0.000 | 0.050 | 0.000 | 14 |
| 比較例4 | 1.000 | 0.950 | 0.000 | 0.000 | 0.050 | 12 |
| 比較例5 | 1.000 | 0.950 | 0.025 | 0.000 | 0.025 | 14 |
| 比較例6 | 1.000 | 0.950 | 0.025 | 0.025 | 0.000 | 37 |
| 比較例7 | 1.000 | 0.950 | 0.000 | 0.025 | 0.025 | 15 |

[0027] In the lithium nickel complex oxide which contains nickel so that clearly from this result the lithium cell of the example 6 of a comparison which used what permuted a part of the nickel from Co and Mn for positive active material -- other example of comparison 1-, although the charge-and-discharge cycle property was improving compared with each lithium cell of 5 and 7 As shown in examples 1-6, a part of the nickel is permuted from Co and Mn. That part was made to permute with aluminum furthermore, and the charge-and-discharge cycle property of each lithium cell which used the positive active material which fulfilled the conditions of this invention was improving remarkably further rather than the lithium cell of the example 6 of a comparison.
[0028] In these examples 7-12 and the examples 8-13 of a comparison (Examples 7-12 and examples 8-13 of a comparison) In producing a positive electrode like the case of the above-

mentioned examples 1-6 and the examples 1-7 of a comparison LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 aluminum3 (OH) It uses. It is made to become a mole ratio as Li:nickel:Co:Mn:aluminum shows in the following table 2, and each lithium cell which became a coin form was produced like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison except it.

[0029] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 2.
[0030]
[Table 2]

| | 正極活物質（モル比） | | | | | サイクル数 |
|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Al | (回) |
| 実施例7 | 1.000 | 0.800 | 0.150 | 0.025 | 0.025 | 201 |
| 実施例8 | 1.000 | 0.800 | 0.025 | 0.150 | 0.025 | 176 |
| 実施例9 | 1.000 | 0.800 | 0.025 | 0.025 | 0.150 | 194 |
| 実施例10 | 1.000 | 0.800 | 0.090 | 0.020 | 0.090 | 190 |
| 実施例11 | 1.000 | 0.800 | 0.090 | 0.090 | 0.020 | 187 |
| 実施例12 | 1.000 | 0.800 | 0.020 | 0.090 | 0.090 | 181 |
| 比較例8 | 1.000 | 0.800 | 0.200 | 0.000 | 0.000 | 19 |
| 比較例9 | 1.000 | 0.800 | 0.000 | 0.200 | 0.000 | 16 |
| 比較例10 | 1.000 | 0.800 | 0.000 | 0.000 | 0.200 | 17 |
| 比較例11 | 1.000 | 0.800 | 0.100 | 0.000 | 0.100 | 18 |
| 比較例12 | 1.000 | 0.800 | 0.100 | 0.100 | 0.000 | 32 |
| 比較例13 | 1.000 | 0.800 | 0.000 | 0.100 | 0.100 | 12 |

[0031] Consequently, it sets to the lithium nickel complex oxide containing nickel like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison. Permuted a part of that nickel from Co and Mn, that part was made to permute with aluminum further, and the charge-and-discharge cycle property of each lithium cell of the examples 7-12 which used the positive active material which fulfills the conditions of this invention was improving remarkably compared with each lithium cell of the examples 8-13 of a comparison.
[0032] Also in these examples 13-20 and the examples 14-19 of a comparison (Examples 13-20 and examples 14-19 of a comparison) In producing a positive electrode like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 aluminum3 (OH) It uses. It is made to become a mole ratio as Li:nickel:Co:Mn:aluminum shows in the following table 3, and each lithium cell which became a coin form was produced like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison except it.
[0033] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 3.
[0034]
[Table 3]

| | 正極活物質（モル比） | | | | | サイクル数 |
|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Al | (回) |
| 実施例13 | 1.000 | 0.700 | 0.250 | 0.025 | 0.025 | 194 |
| 実施例14 | 1.000 | 0.700 | 0.050 | 0.200 | 0.050 | 124 |
| 実施例15 | 1.000 | 0.700 | 0.050 | 0.050 | 0.200 | 135 |
| 実施例16 | 1.000 | 0.700 | 0.125 | 0.050 | 0.125 | 197 |
| 実施例17 | 1.000 | 0.700 | 0.125 | 0.125 | 0.050 | 193 |
| 実施例18 | 1.000 | 0.700 | 0.050 | 0.125 | 0.125 | 189 |
| 実施例19 | 1.000 | 0.700 | 0.075 | 0.075 | 0.150 | 184 |
| 実施例20 | 1.000 | 0.700 | 0.075 | 0.150 | 0.075 | 193 |
| 比較例14 | 1.000 | 0.700 | 0.300 | 0.000 | 0.000 | 21 |
| 比較例15 | 1.000 | 0.700 | 0.000 | 0.300 | 0.000 | 27 |
| 比較例16 | 1.000 | 0.700 | 0.000 | 0.000 | 0.300 | 22 |
| 比較例17 | 1.000 | 0.700 | 0.150 | 0.000 | 0.150 | 25 |
| 比較例18 | 1.000 | 0.700 | 0.150 | 0.150 | 0.000 | 20 |
| 比較例19 | 1.000 | 0.700 | 0.000 | 0.150 | 0.150 | 21 |

[0035] Consequently, in the lithium nickel complex oxide containing nickel, permuted a part of that nickel from Co and Mn, that part was made to permute with aluminum further, and the charge-and-discharge cycle property of each lithium cell of the examples 13-20 which used the positive active material which fulfills the conditions of this invention was improving remarkably compared with each lithium cell of the examples 14-19 of a comparison.
[0036] Moreover, when each lithium cell of examples 13-20 was compared, compared with the lithium cell of examples 14 and 15 with which the amount of Mn permuted by nickel or aluminum became 0.2 mols, the charge-and-discharge cycle property of each lithium cell of examples 13, 16-20 with which the amount of Mn permuted by nickel or aluminum became less than 0.2 mols was improving further.
[0037] Also in these examples 21-31 and the examples 20-25 of a comparison (Examples 21-31 and examples 20-25 of a comparison) In producing a positive electrode like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 aluminum3 (OH) It uses. It is made to become a mole ratio as Li:nickel:Co:Mn:aluminum shows in the following table 4, and each lithium cell which became a coin form was produced like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison except it.
[0038] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 4.
[0039]
[Table 4]

| | 正極活物質（モル比） | | | | | サイクル数 |
|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Al | (回) |
| 実施例21 | 1.000 | 0.550 | 0.400 | 0.025 | 0.025 | 197 |
| 実施例22 | 1.000 | 0.550 | 0.075 | 0.300 | 0.075 | 130 |
| 実施例23 | 1.000 | 0.550 | 0.075 | 0.075 | 0.300 | 134 |
| 実施例24 | 1.000 | 0.550 | 0.200 | 0.050 | 0.200 | 132 |
| 実施例25 | 1.000 | 0.550 | 0.200 | 0.200 | 0.050 | 125 |
| 実施例26 | 1.000 | 0.550 | 0.050 | 0.200 | 0.200 | 130 |
| 実施例27 | 1.000 | 0.550 | 0.300 | 0.025 | 0.125 | 207 |
| 実施例28 | 1.000 | 0.550 | 0.300 | 0.125 | 0.025 | 199 |
| 実施例29 | 1.000 | 0.550 | 0.125 | 0.200 | 0.125 | 126 |
| 実施例30 | 1.000 | 0.550 | 0.125 | 0.125 | 0.200 | 134 |
| 実施例31 | 1.000 | 0.550 | 0.150 | 0.150 | 0.150 | 190 |
| 比較例20 | 1.000 | 0.550 | 0.450 | 0.000 | 0.000 | 22 |
| 比較例21 | 1.000 | 0.550 | 0.025 | 0.400 | 0.025 | 20 |
| 比較例22 | 1.000 | 0.550 | 0.025 | 0.025 | 0.400 | 23 |
| 比較例23 | 1.000 | 0.550 | 0.225 | 0.000 | 0.225 | 28 |
| 比較例24 | 1.000 | 0.550 | 0.225 | 0.225 | 0.000 | 30 |
| 比較例25 | 1.000 | 0.550 | 0.000 | 0.225 | 0.225 | 29 |

[0040] Consequently, in the lithium nickel complex oxide containing nickel, permuted a part of that nickel from Co and Mn, that part was made to permute with aluminum further, and the charge-and-discharge cycle property of each lithium cell of the examples 21-31 which used the positive active material which fulfilled the conditions of this invention was improving remarkably.
[0041] Moreover, when each lithium cell of examples 21-31 was compared, compared with each lithium cell of examples 22-26, and 29 and 30 with which the amount of Mn permuted by nickel or aluminum became 0.2 mols or more, the charge-and-discharge cycle property of each lithium cell of examples 21, 27, 28, and 31 with which the amount of Mn permuted by nickel or aluminum became less than 0.2 mols was improving further.
[0042] Moreover, even if it was the case where the thing which some nickel was permuted [ thing ] from Co and Mn and made that part permute with aluminum further like the examples 21 and 22 of a comparison was used for positive active material, the charge-and-discharge cycle property is not improved in what there are many amounts of Mn permuted by nickel or aluminum as 0.4 mols, and does not fulfill the conditions of this invention.
[0043] In producing a positive electrode also in these examples 26-36 of a comparison (Examples 26-36 of a comparison) They are LiOH and nickel (OH)2 like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison. Co2 (OH) Mn 2O3 aluminum3 (OH) It uses. It is made to become a mole ratio as Li:nickel:Co:Mn:aluminum shows in the following table 5, and each lithium cell which became a coin form was produced like above-mentioned examples 1-6 and example 1 of comparison - 7 case except it.
[0044] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 5.
[0045]
[Table 5]

| | 正極活物質（モル比） | | | | | サイクル数 |
|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Al | (回) |
| 比較例26 | 1.000 | 0.500 | 0.500 | 0.000 | 0.000 | 19 |
| 比較例27 | 1.000 | 0.500 | 0.050 | 0.400 | 0.050 | 25 |
| 比較例28 | 1.000 | 0.500 | 0.050 | 0.050 | 0.400 | 37 |
| 比較例29 | 1.000 | 0.500 | 0.250 | 0.000 | 0.250 | 38 |
| 比較例30 | 1.000 | 0.500 | 0.250 | 0.250 | 0.000 | 29 |
| 比較例31 | 1.000 | 0.500 | 0.000 | 0.250 | 0.250 | 27 |
| 比較例32 | 1.000 | 0.500 | 0.400 | 0.050 | 0.050 | 29 |
| 比較例33 | 1.000 | 0.500 | 0.200 | 0.200 | 0.100 | 27 |
| 比較例34 | 1.000 | 0.500 | 0.100 | 0.200 | 0.200 | 31 |
| 比較例35 | 1.000 | 0.500 | 0.200 | 0.100 | 0.200 | 35 |
| 比較例36 | 1.000 | 0.500 | 0.167 | 0.167 | 0.166 | 32 |

[0046] Consequently, each lithium cell of these examples 26-36 of a comparison Compared with the lithium cell of each above-mentioned example, the charge-and-discharge cycle property is low. Like each lithium cell of the examples 27, 28, 32-36 of a comparison Even if it uses the positive active material which a part of the nickel was permuted [ positive active material ] from Co and Mn, and made the part permute with aluminum further in the lithium nickel complex oxide containing nickel The charge-and-discharge cycle property is not improved in what there is much total quantity of Co, Mn, and aluminum which permute nickel as 0.5 mols, and does not fulfill the conditions of this invention.

[0047] In these examples 32-46 and the examples 37-44 of a comparison (Examples 32-46 and examples 37-44 of a comparison) In producing a positive electrode like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 While using aluminum3 (OH) It is made to make the compound shown in the following table 6 add instead. When the element in this compound is set to M, it is made for Li:nickel:Co:Mn:M to be set to 1:0.95:0.04:0.005:0.005 by the mole ratio. Except it Each lithium cell which became a coin form was produced like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison.

[0048] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 6.

[0049]

[Table 6]

| | 添加化合物の種類 | サイクル数（回） |
|---|---|---|
| 実施例３２ | $Fe(OH)_3$ | １４５ |
| 実施例３３ | $V_2O_5$ | １２４ |
| 実施例３４ | $Y_2O_3$ | １５５ |
| 実施例３５ | $CrO_3$ | １３４ |
| 実施例３６ | $Ga_2O_3$ | １３６ |
| 実施例３７ | $GeO_2$ | １１９ |
| 実施例３８ | $B_2O_3$ | １４７ |
| 実施例３９ | $SiO \cdot xH_2O$ | １２９ |
| 実施例４０ | $Tl(OH)_4$ | １５７ |
| 実施例４１ | $Cu(OH)_2$ | １４２ |
| 実施例４２ | $ZnO \cdot H_2O$ | １４４ |
| 実施例４３ | RbOH | １２９ |
| 実施例４４ | $Rh_2O_3$ | １４２ |
| 実施例４５ | $PdO \cdot H_2O$ | １３５ |
| 実施例４６ | $WO_2$ | １３０ |
| 比較例３７ | $Sc_2O_3$ | １５ |
| 比較例３８ | $Cd(OH)_2$ | １３ |
| 比較例３９ | $Sr(OH)_2$ | ２２ |
| 比較例４０ | $ZrO_2$ | １５ |
| 比較例４１ | $MoO_2$ | １１ |
| 比較例４２ | $Nb_2O_5$ | ２１ |
| 比較例４３ | $Sn(OH)_2$ | １５ |
| 比較例４４ | $Ag_2O$ | １３ |

[0050] Consequently, it sets to the lithium nickel complex oxide containing nickel. Permute a part of the nickel from Co and Mn, and the element chosen from the group which consists of Fe, V, Y, Cr, Ga, germanium, B, Si, Ti, Cu, Zn, Rb, Rh, Pd, and W is made to permute a part of the nickel further. Compared with each lithium cell of the examples 37-44 of a comparison which made some nickel permute, the charge-and-discharge cycle property of each lithium cell of the examples 32-46 which used the positive active material which fulfilled the conditions of this invention was improving remarkably by elements other than the above-mentioned element.
[0051] In these examples 47 and 48 (Examples 47 and 48) In producing a positive electrode like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison LiOH and nickel2 (OH) Co2 (OH) Mn 2O3 While using aluminum3 (OH) To instead of, it is Y2 O3. CrO3 Use and it is made to become a mole ratio as Li:nickel:Co:Mn:Y:Cr shows in the following table 7. Except it Each lithium cell which became a coin form was produced like the case of the above-mentioned examples 1-6 and the examples 1-7 of a comparison.
[0052] And also about each of these lithium cells, like the above-mentioned case, it asked for the number of cycles until discharge capacity is less than 90% of initial discharge capacity, and the result was shown according to the following table 7.
[0053]
[Table 7]

| | 正極活物質（モル比） | | | | | | サイクル数 |
|---|---|---|---|---|---|---|---|
| | Li | Ni | Co | Mn | Y | Cr | (回) |
| 実施例47 | 1.000 | 0.950 | 0.040 | 0.005 | 0.003 | 0.002 | 142 |
| 実施例48 | 1.000 | 0.950 | 0.040 | 0.005 | 0.002 | 0.003 | 130 |

[0054] Consequently, in the lithium nickel complex oxide containing nickel, permuted a part of that nickel from Co and Mn, two elements of Y and Cr were made to permute that part further, and the charge-and-discharge cycle property was improving remarkably compared with the lithium cell of each example of a comparison also in each lithium cell of the examples 47 and 48 which used the positive active material which fulfilled the conditions of this invention.
[0055] In addition, in these examples 47 and 48, in the lithium nickel complex oxide containing nickel, although the example which a part of the nickel was permuted [ example ] from Co and Mn, and made the part permute by two elements of Y and Cr further was only shown Also when other two or more elements are made to choose and permute out of Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, above-mentioned Pd, and above-mentioned W, the almost same result is obtained.
[0056] Moreover, in each above-mentioned example, although the example of the lithium cell which became a coin form was shown, especially, it is not limited to the above configurations, but can form in various configurations, such as a cylindrical shape and a square shape, and the configuration of the cell in this invention can also use a solid electrolyte as nonaqueous electrolyte.
[0057] Furthermore, in the lithium nickel complex oxide containing nickel, a part of the nickel is permuted from Co and Mn. The raw material used when making the element chosen from the group which consists of Fe, V, Y, Cr, Ga, germanium, B, Si, Ti, Cu, Zn, Rb, Rh, Pd, and W permute the part furthermore It is not limited to the above oxides or hydroxides, but which raw materials, such as a nitride, a nitrate, a carbonate, a sulfate, acetate, and an oxalate, may be used.
[0058]
[Effect of the Invention] In a nonaqueous electrolyte rechargeable battery [ in / as explained in full detail above / this invention ] As metallic compounds in the positive electrode, some nickel in the lithium nickel complex oxide containing nickel is permuted from Co and Mn. Furthermore, a part of this nickel is permuted at least by a kind of element chosen from Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W. Lia Cob MncMd nickel1-(b+c+d) O2 It is expressed. At least by a kind of element chosen from the group which M becomes from Y, B, aluminum, Si, Ti, Fe, V, Cr, Cu, Zn, Ga, germanium, Rb, Rh, Pd, and W Since a-d used $0< a<1.2$, $0< b<0.5$, $0< c<0.4$, $0< d<0.4$, and the thing that fulfills the conditions of $0<b+c+d<0.5$, while the charge-and-discharge property which repeatability fixed well is acquired There are few falls of cell capacity and the nonaqueous electrolyte rechargeable battery excellent in the charge-and-discharge cycle property came to be obtained.

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[Translation done.]

* NOTICES *



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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]
[Drawing 1] It is the cross-section explanatory view having shown the internal structure of each lithium cell of the example of this invention, and the example of a comparison.
[Description of Notations]
1 Positive Electrode
2 Negative Electrode

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DRAWINGS

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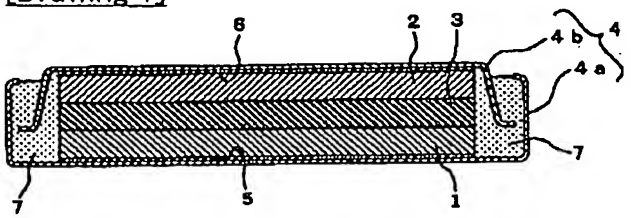
[Drawing 1]

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[Translation done.]